

POLYACETAL RESINS WITH REDUCED
FORMALDEHYDE ODOR

5 **CROSS REFERENCE TO RELATED APPLICATIONS**

This application is a continuation of U.S. application SN 09/287,432, filed on April 7, 1999, which is incorporated as a part hereof.

10

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a novel polyacetal resin composition, and articles molded therefrom, which has excellent
15 heat stability, air oven aging and moldability as well as a considerably reduced formaldehyde odor for packaged resins and molded parts.

Background

20 Polyacetal resins, which are prepared by polymerizing a starting material mainly comprising formaldehyde monomer or trioxane, a trimer of formaldehyde, exhibit excellent mechanical and physical properties, such as tensile strength, stiffness, as well as fatigue resistance, sliding resistance, chemical resistance, and
25 the like. The resins are used extensively in various applications as an engineering plastic material due to their excellent physical properties (such as mechanical and electrical properties) and chemical properties. However, the resins at times may evolve

traces of formaldehyde from which they were made, even at room temperature. Similarly, molded articles made from polyacetal resins may also evolve traces of formaldehyde, which may make molded parts to be less desirable in some circumstances.

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US Patent No. 5,866,671 discloses polyacetal compositions containing acidic hydantoin and imidazole derivatives with reduced odor levels.

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There is still a demand for means to reduce the formaldehyde odor in polyacetal resins as well as that which may arise in articles molded from polyacetal resins.

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SUMMARY OF THE INVENTION

The present inventors have surprisingly found a novel composition comprising:

- a) a polyacetal resin; and
 - b) a sufficient amount of at least an odor-reducing additive to
- 20 reduce the formaldehyde concentration of the resin to less than 50%. The odor-reducing additive is selected from the group consisting of: (i) a low molecular weight primary or secondary amino compound of low volatility, containing at least one amino group and two or more carbon atoms and having a weak basicity of
- 25 P_{kb} in the range of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid, and mixtures thereof.

The invention also relates to a novel composition comprising:
a) a polyacetal resin; a sufficient amount of at least b) an odor-reducing additive selected from the group consisting of: (i.) a low molecular weight primary or secondary amino compound of low volatility, containing at least one amino group and two or more carbon atoms and having a weak basicity of P_{Kb} in the range of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic acid; and c) a weak acidic organic cyclic compound having an active imino, to provide a synergistic effect in reducing the formaldehyde odor of at least in half.

DETAILED DESCRIPTION OF THE INVENTION

Polyacetal Resins

The polyacetal base resin that may be used in the compositions of the present invention is a high-molecular weight polymer comprised of repeating oxymethylene units ($-CH_2O-$) which may be selected from among polyoxymethylene homopolymers, copolymers (including block copolymers) and terpolymers comprising oxymethylene units and a minor amount of other constituent units.

The polyacetals used in the compositions of the present invention may, moreover, be linear, branched or crosslinked, with terminal groups thereof being either not protected or being protected. The polyacetal resin will generally have a number average molecular weight in the range of 5,000 to 100,000,

preferably 10,000 to 70,000. The molecular weight can conveniently be measured by gel permeation chromatography in m-cresol at 160° C. using a Du Pont PSM bimodal column kit with nominal pore size of 60 and 1000 Angstrom.

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The polyacetal used in the present invention can be either a homopolymer, a copolymer or a mixture thereof. The preferred homopolymer is generally prepared by the polymerization of anhydrous formaldehyde or a cyclic trimer thereof, i.e., trioxane.

- 10 Generally, the homopolymer is stabilized against thermal decomposition by end-capping with a suitable moiety having greater stability as compared to the oxymethylene units. The preferred copolymer on the other hand is a high-molecular weight polymer comprising between about 85 to 99.9% of repeating
- 15 oxymethylene units randomly interspersed with higher oxyalkylene units (e.g., having two or more adjacent carbon atoms).

Copolymers can contain one or more comonomers, such as those generally used in preparing polyacetal compositions.

- 20 Comonomers more commonly used include alkylene oxides of 2-12 carbon atoms and their cyclic addition products with formaldehyde. The quantity of comonomer will not be more than 20 weight percent, preferably not more than 15 weight percent, and most preferably about 2 weight percent. The most preferred
- 25 comonomer is ethylene oxide. Generally polyacetal homopolymer is preferred over copolymer because of its greater stiffness. Preferred polyacetal homopolymers include those whose terminal hydroxyl

groups have been end-capped by a chemical reaction to form ester or ether groups, preferably acetate or methoxy groups, respectively.

Additives

5 The odor-reducing additives of the present invention include:
i) a water-soluble, low molecular weight primary or secondary
amino compound, containing at least one amino group and two or
more carbon atoms and having a weak basicity of P_{kb} in the range
of 2 – 8; (ii) succinimide; (iii) anthranilic acid; (iv) 4-amino benzoic
10 acid, and mixtures thereof.

 With respect to the water-soluble, low molecular weight
primary or secondary amino compounds containing at least one
amino group and two or more carbon atoms, no particular
15 limitation is imposed on the number of amino group(s). The
amino compounds can be an aliphatic, alicyclic, aromatic or
heterocyclic group having two or more carbon atoms. The amino
compounds may contain one or more groups other than amino
group(s), for example, hydroxyl, ester, ether, carboxyl, carbonyl,
20 amido, imido, sulfonic, carboxamido, imino and/or unsaturated
groups.

 The water-soluble, low molecular weight primary or
secondary amino compounds are characterized by being weak
25 bases, i.e., having have a basicity p_{kb} 's ranging from about 2 to 8,
preferably being very weak bases, i.e., having have a basicity p_{kb} 's
ranging from about 4 to 8.

The water-soluble, low molecular weight primary or secondary amino compounds are further characterized as having a low volatility, i.e., the boiling point of the amino compounds should be as follows: $T_{bp} > T_m - 60^\circ\text{C}$, where T_{bp} is the boiling point of the amino compounds and T_m is the melting point of the polyacetal base resin.

Specific examples of such water-soluble, low molecular weight primary or secondary amino compounds include, but are not limited to, e.g., monoethanolamine, diethanolamine, tris(hydroxymethyl)aminomethane, alkyl aminobenzoates such as ethyl p-aminobenzoate, methyl anthranilate and butyl m-aminobenzoate, 2-amino-2-ethyl-propanediol and 2-amino-2-methyl-propanol.

Tris(hydroxymethyl)aminomethane, ethyl p-aminobenzoate, 2-amino-2-ethyl-propanediol and 2-amino-2-methyl-propanol are preferred for use as water-soluble, low molecular weight primary or secondary amino compounds in accordance with this invention. Tris(hydroxymethyl)aminomethane and ethyl p-aminobenzoate are most preferred.

The amount of the odor-reducing additives to added to the compositions of the present invention should be in a sufficient amount to reduce the formaldehyde level of the resin or its molded parts in half. The amount of additives is about 0.01 - 10 in parts by weight, preferably 0.02 - 5 by weight, and most preferably

0.05 – 2 parts by weight, per 100 parts by weight of the polyacetal resin.

Other Additives

5 The composition of the present invention can further contain, one or more ordinary additives including: lubricants; nucleating agents; mold release agents; antistatic agents; surfactants; organic polymeric materials; inorganic, organic, fibrous, granular or platy fillers, anti-oxidants, pigments,
10 colorants, carbon black, reinforcing agents and fillers such as a glass fiber, etc., in such an amount as not to negate the effects of this invention.

 Representative lubricants that may be used include, but are
15 not limited to, silicone types such as dimethylpolysiloxanes and their modifications; oleic acid amides; alkyl acid amides, e.g., stearic acid amide types; bis-fatty acid amid type lubricants such as bisamides; non-ionic surfactant type lubricants; hydrocarbon type lubricants waxes, chlorohydrocarbons, fluorocarbons; fatty
20 acid type lubricants including oxy-fatty acid; ester-type lubricants including lower alcohol esters of fatty acids; alcohol type lubricants including polyvalents, polyglycols, polyglycerols; and metal soaps such as lauric acid, stearic acid, etc., with metals.

25 Also, it is desirable to add antioxidant to prevent oxidative deterioration of the resin. Hindered phenol type antioxidants are preferred, and those antioxidants with melting point higher than 100°C, especially above 120°C, are most preferred.

It is also desirable to add heat stabilizers to the composition of this invention as formaldehyde scavengers such as: polyamide resins, amide compounds, urea derivatives and triazine derivatives.

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Suitable polyamide resins include polyamide compounds, especially nylon terpolymers, hydroxy containing polymers, and nonmelting nitrogen or hydroxy containing compounds, e.g., polyamide 6, polyamide 6/12 copolymer, polyamide 6/66/610
10 terpolymer, polyamide 6/66/612 terpolymer, ethylene-vinyl alcohol copolymer, acrylamide (co)polymer, acrylamide/N,N-methylenebis-acrylamide copolymer, stearic acid monoglyceride and poly beta alanine and the like.

15 Suitable amide compounds are stearic acid amide, oleic acid amide, erucic acid amide, ethylenediamine-distearic acid amide, ethylenediamine-dibehenic acid amide, hexamethylenediamine-distearic acid amide, ethylenediamine-dioleic acid amide, ethylenediamine-dierucic acid amide, xylylenediamine-dierucic
20 acid amide, di(xylylenediamine-stearic acid amide)sebacic acid and the like.

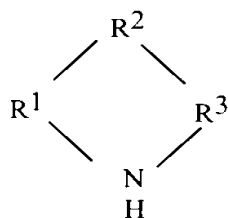
Suitable urea derivatives are N-phenylurea, N,N'-diphenylurea,
25 N-phenylthiourea, N,N'-diphenylthiourea and the like.

Suitable triazine derivatives are melamine, benzoguanamine, N-phenylmelamine, N,N'-diphenylmelemine, N-methylolmelamine,

N,N'-trimethylolmelamine, 2,4-diamino-6-cyclohexyltriazine, and the like.

These heat stabilizer may be used individually or in
5 combination. Of these, nylon 66, poly beta - alanine,
ethylenediamine-distearic acid amide,
ethylenediamine-dibehenic acid amide, ethylenediamine-dierucic
acid amide,
di(xylylenediamine-stearic acid amide)sebacic acid amide are
10 preferred.

The composition may also contain an organic cyclic
compound having an active imino group according to the formula:



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wherein R^1 , R^2 and R^3 represent divalent organic radicals. The
organic cyclic compound having an active imino group may be
used in an amount sufficient for the composition to have a
20 formaldehyde concentration at room temperature of about less
than 50% of the formaldehyde concentration of a polyacetal
composition free of the odor-reducing additive described above and
the organic cyclic compound having an active imino group.

Preparation

The compositions of the present invention can be prepared by any means of compounding. The additives can be added as dry powders, as concentrates ("master-batch"), as dispersions, or as solutions. One preferred method of incorporation involves adding the odor-reducing additives to polyacetal resin pellets to coat the pellets, and thereby mixing the mixtures in an extruder or injection molder. In addition, the odor-reducing additives may be compounded into the polyacetal resin at the same time that other additives, such as thermal stabilizers, antioxidants, fillers, etc., are compounded therein. The additives may be added in the form of particle or in the molten state.

Molded parts of these polyacetal resin compositions may be formed by any molding process conventional in the plastics-forming art, including compression molding, vacuum forming, injection molding, extrusion molding, blow molding, rotary molding, melt spinning, and heat molding. Injection molding is especially preferred. During injection molding of the claimed compositions, mold deposits attached to the mold were evaluated visually and were hardly observed or not found at all.

Examples

In the Examples and Comparative Examples, the characteristics of the acetal resin compositions and moldings were determined as follows:

Thermal Stability Test. Two grams of resin pellets were melted for 30 minutes at 250°C in a nitrogen atmosphere. The formaldehyde gas generated by the decomposition of the resin was introduced into a 4% aqueous sodium bisulfite solution, followed
5 by titration with a 0.1 N hydrochloric acid (HCl). The amount of formaldehyde gas generated (TEF) is expressed by the following formula:

Amount of formaldehyde formed (%) = $30.03 \text{ NV/S} \times 100$
10 wherein V was the amount of HCl, in ml, required for titrating after 30 minutes, N was the normality, in ml, of HCl, S was the amount of sample, in grams, and 30.03 was the molecular weight of formaldehyde.

15 Odor Test 1 – Pellets: 100 g of resin pellets were sealed in a 300 ml polyethylene containers and kept at various temperatures: room temperature, 50°C and 80°C. At the start of the test, then after 1 and 2 hours respectively, 10 ml of gas was removed from the containers using a syringe and formaldehyde concentration
20 was measured using a gas-phase measuring device made by Lion Company called Formaldemeter Mark II.

Odor Test 2 – Pellets: Resin pellets were stored at room temperature in sealed 50-lb. bags made out of polyethylene. Gas
25 samples were tested by removing 1cc. gas from the sealed bags and formaldehyde concentration was measured using the gas-phase measuring device Formaldemeter Mark II.

Odor Test 3 – Molded Tensile-bar tests: 1/16" Tensile-bars were molded from a control composition as well as the claimed compositions. The tensile bars were stored at room temperature in sealed 1 gallon polyethylene containers. Gas samples were tested
5 by removing 1cc. gas from the sealed containers and formaldehyde levels were measured using a Formaldemeter Mark II.

Odor Test 4 – Molded part test: molded parts were molded from the claimed compositions, kept in sealed 300 ml polyethylene
10 containers at various temperatures: 50°C and 80°C. Gas samples were tested by removing 1cc. gas from the sealed containers and formaldehyde levels were measured using a Formaldemeter Mark II by the Lion Company.

15 Components: The polyacetal resins used in the Examples below were:

1. Polyacetal A available from E. I. du Pont de Nemours and Company of Wilmington, Delaware, USA ("DuPont"), having a number average molecular weight of about 37,000;
- 20 2. Polyacetal B available from DuPont, having a number average molecular weight of about 30,000;
3. Polyacetal C also available from DuPont, having a number average molecular weight of about 77,000; and
4. Polyacetal D, available from Polyplastics, Japan, under the
25 tradename Duracon® M25.

The additives used in the Examples are as listed in the tables below. In the Examples, THAM is tris(hydroxymethyl)aminomethane, EPA is ethyl p-aminobenzoate,

AEPD is 2-amino-2-ethyl-propanediol and AMP is 2-amino-2-methyl-propanol.

Preparations: The polyacetal resin was mixed with the additives in an extruder and the resultant resin was pelletized, and in some instances, formed into molded parts. The samples were evaluated by the Thermal Heat Stability test and the various Odor Tests. Comparative Examples were those obtained by processing similar polyacetal without any odor-reducing additives at all.

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The results of evaluation are listed in the tables below, demonstrating that the examples using the additives of the present invention were able to suppress the formaldehyde odors in resin without severely adversely affecting the melt stability of the resins.

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In the first set of experiments, polyacetal B was used and the formaldehyde levels were measured using the Thermal Stability test as well as the Odor Test 1 (pellets in 300 ml PE bottle):

Table 1

Example	Wt. % additive	Additive	TEF	ppm CHCHO ppm initial	ppm CHCHO 50°C / 1hr	ppm CHCHO 80°C / 1hr
Com 1-1	-	None	0.1 5	19.5	84	> 85
1-2	0.05	EPA	0.1 3	6.8	30.9	75.4
1-3	0.2	EPA	0.1 2	0.5	3.3	13.8
1-4	0.5	EPA	0.1 3	0.3	1.3	7.3
1-5	0.2	THAM	0.2 3	0.5	1.6	3.0

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In the next set of experiments, polyacetal A was used and the formaldehyde levels were measured using the Thermal Stability test as well as the Odor Test 2 (50 lb. PE sealed bags).

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Table 2

Example	Wt. % additive	Additives	TEF	Ppm CHCHO 19°C /3 day	Ppm CHCHO 23°C /7 day	ppm CHCHO 24°C/23 day
Compare 2-1	0.0	None	0.47	34.4	56.0	44.8
2-2	0.2	THAM	0.83	0.3	0.4	0.4
2-3	0.2	Theophyline	2.59	2.9	0.7	1.5
2-4	0.2	Succinimide	1.12	0.9	1.1	1.2
2-5	0.2	Anthranilamide	1.33	0.3	0.3	0.5
2-6	0.2	Glycine anhydride	-	7.6	12.0	15.1
2-7	0.2	Anthranilic acid	2.37	0.3	1.2	2.0
2-8	0.2	4-amino benzoic acid	-	1.6	5	13.1
2-9	0.2	Uracil	0.92	1.7	3.2	6.1
2-10	0.2	Barbituric acid	-	0.3	0.5	0.5

In the third set of experiments, polyacetals C and D were used and the formaldehyde levels were measured via Odor Tests 1 (pellets in 300 ml PE bottle):

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Table 3

Example	Polyacetal Resin	Wt. % Additive	Additive	ppm CH ₂ O 23C/ 1hr	ppm CH ₂ O 50C/ 1hr	ppm CH ₂ O 80C/ 1hr
Com 3-1	C	-	None	12.7	70.8	> 86
3-2	C	0.05	THAM	0.4	1.7	1.0
3-3	C	0.05	AMP	1.2	12.2	63.8
3-4	C	0.05	AEPD	0.4	2.0	2.8
3-5	D	0.05	THAM	0.1	1.9	2.0

In table 4, polyacetal A was used and the formaldehyde levels were measured via Odor Tests 2 (50 lb. sealed bags) and 3 (tensile-bar samples). In some of the examples, an acidic organic cyclic compound having an active imino such as 5,5-dimethylhydantoin (DMH) was added to the additive of the present invention.

15 The combination of the odor-reducing additives of the invention with the weak acidic imino was found to have a synergistic effect in reducing formaldehyde odor:

Table 4

Example	Wt. % additive	Additive	TEF	ppm CH ₂ O 3 days	ppm CH ₂ O 7 days	ppm CH ₂ O 21days	ppm CH ₂ O T-Bars 1day
Com 4-1	-	None	0.69	34.4	95.6	80	383.2
4-2	0.05	DMH	0.63	5.1	5.3	3.8	147
4-3	0.1	DMH	0.56	5.2	3.3	3	25.6
4-4	0.2	DMH	0.64	2.6	1.8	1.8	16
4-5	0.2	THAM	-	-	0.4	0.4	16
4-6	0.1	50% THAM/ 50% DMH	0.85	0.3	0.3	0.4	12.6
4-7	0.2	50% THAM/ 50% DMH	0.73	0.3	0.3	0.3	7.1

In another set of examples, polyacetal B was used and the formaldehyde levels were measured using Odor Test 1 (pellets in PE bottles):

Table 5

Example	Wt. % additive	Additive	ppm CH ₂ O 23C/ 1hr	ppm CH ₂ O 50C/1hr	ppm CH ₂ O 80C/ 1hr
Compare 5-1	-	None	19.5	84	> 85
5-2	0.05	ethyl p-aminobenzoate	6.8	30.9	75.4
5-3	0.2	ethyl p-aminobenzoate	0.5	3.3	13.8
5-4	0.5	ethyl p-aminobenzoate	0.3	1.3	7.3
5-5	0.2	DMH	0.8	3.9	16.6
5-6	0.2	THAM	0.5	1.6	3.0
5-7	0.1	THAM	0.5	1.4	3.3
5-8	0.1	50% THAM/50% DMH	0.5	4.7	11.7

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The examples were repeated with 30 g of molding parts from polyacetal B, and the formaldehyde levels were measured using Odor Test 4 (molded parts in 300 ml PE bottle), confirming the synergistic effect of a combination of the odor-reducing additives of

the invention with a weak acidic organic cyclic compound having an active imino such as 5,5-dimethylhydantoin (DMH):

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Table 6

Example	Wt. % additive	Additive	Ppm CH ₂ O 50 C / 1hr	ppm CH ₂ O 80 C / 1hr
Compare 6-1	-	None	53.8	> 85
6-2	0.05	Ethyl p-aminobenzoate	58.7	> 85
6-3	0.2	Ethyl p-aminobenzoate	45.2	60.9
6-4	0.5	Ethyl p-aminobenzoate	35.7	32.4
6-5	0.2	DMH	30.6	42.9
6-6	0.2	THAM	67.1	> 85
6-7	0.1	THAM	83	> 85
6-8	0.1	50% THAM/ 50% 5,5- DMH	10.4	38.1

As is apparent from the foregoing description, the materials prepared and procedures followed relate only to specific
 10 embodiments of the broad invention. While forms of the invention have been illustrated and described, modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby.